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(56) Documents Cited

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(54) Abstract Title

Removal of mercury from hydrocarbons using organic sulphur compounds or amalgam-forming metals

(57) A process for purification of hydrocarbons comprises removing mercury by contact with a solid sorbent comprising an organic sulfur compound and/or a metal capable of amalgamation with mercury.

The mercury-removal compound may be supported on silica.

Preferably the organic sulfur compound is an alkylthiol, arylthiol, polythiol or thioamide. The amalgam-forming metal may be gold.

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Fig.1

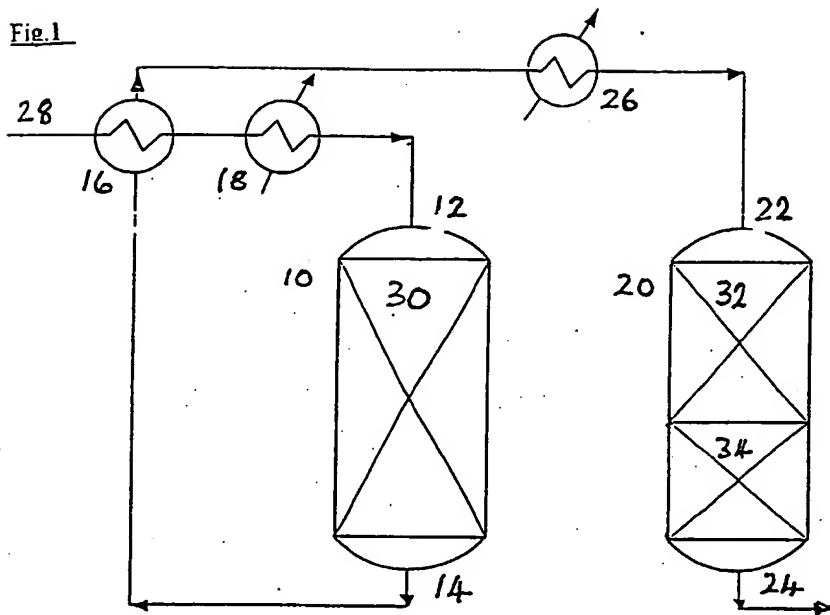


Fig.2

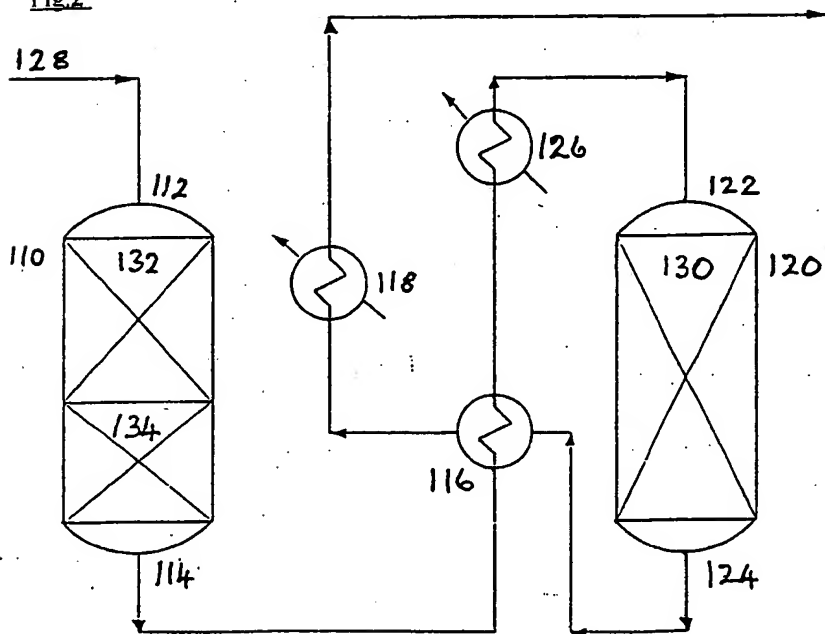
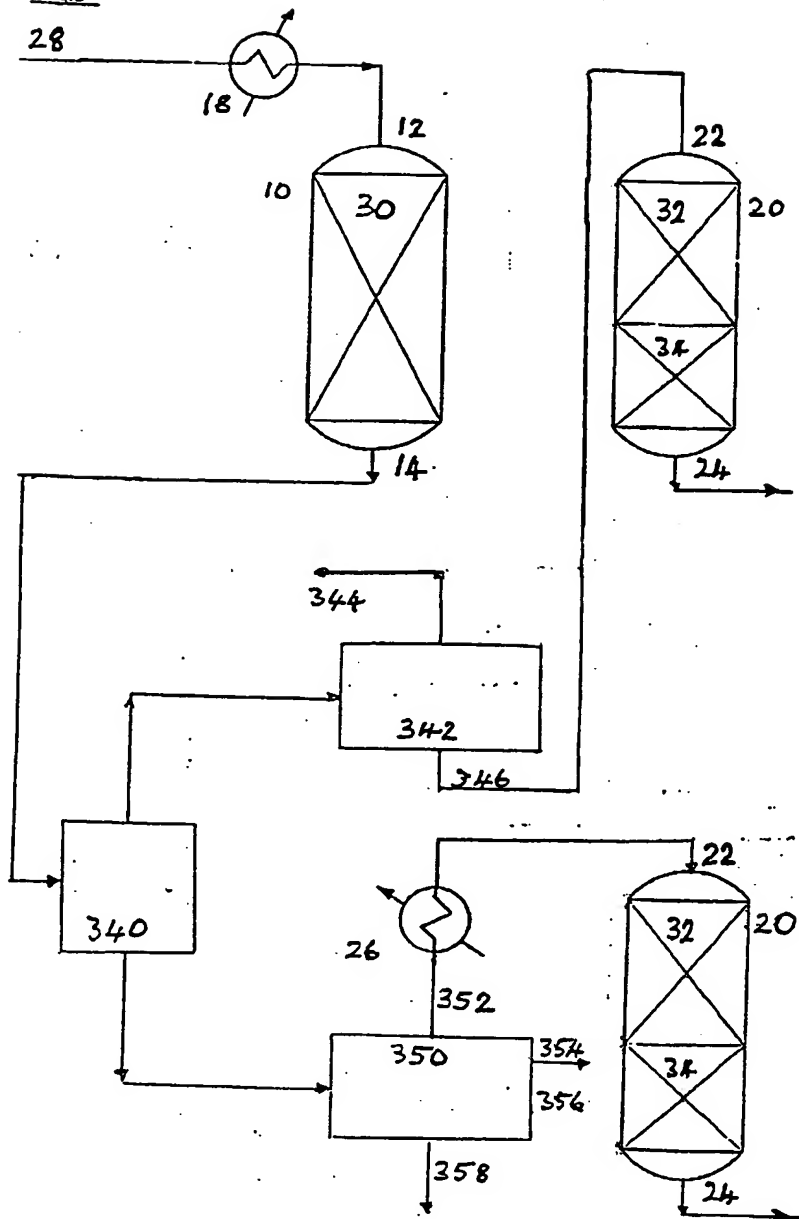


Fig.3



PURIFICATION OF HYDROCARBONS

THIS INVENTION relates to a process for purification of hydrocarbons.

Hydrocarbons to be used as fuels or process feedstocks commonly contain small quantities of mercury as inorganic or organic compounds or in elemental form. As well as being environmentally hazardous, mercury may be harmful in process use. For example precious metal catalysed processes are poisoned by mercury; and the presence of even small traces of mercury in the feed to cryogenic separation leads to the failure of the aluminium equipment used. It has been proposed to remove mercury by contacting with a sorbent based on activated carbon, but high capacity and long process runs are difficult to achieve.

ACCORDING TO THE INVENTION a process for purification of hydrocarbons is characterised by removing mercury by contact with a solid sorbent comprising an organic sulfur compound and/or a metal capable of amalgamation with mercury.

The invention will be illustrated by the accompanying drawings of schematic flowsheets, in which:

Figure 1 illustrates a process using a high temperature mercury removal stage followed by a low temperature stage;

Figure 2 illustrates a process using a low temperature stage mercury removal followed by a high temperature stage;

Figure 3 shows integration of the fig. 1 process into a condensate treatment system producing 2 fractions possibly differing in level of mercury freedom; and

In this specification percentage compositions of solids are by weight as oxides stable to ambient atmosphere, unless otherwise stated. The term 'sorbent' includes adsorbent and absorbent. The term 'mercury' includes the free metal and compounds thereof, whichever may be initially present.

The process preferably comprises the further steps of replacing the spent sorbent and recovering the mercury and, if applicable, amalgam, from it. Such recovery may be carried out by the process operator's organisation or, more conveniently, by a firm specialising in such recovery.

The sulfur compound-containing sorbent is characterised as follows:

- (i) a high surface area support, suitably 50-500, e g 100-300, m^2g^{-1} ;
- (ii) sulfur compound exerting low vapour pressure at the temperature at which the

process is to be operated, by virtue of high boiling point or strong physical or chemical sorption.

The support is preferably silica, for example silica gel or pelleted kieselguhr or fumed silica. The sorbent is preferably dehydrated before applying the sulfur compound to it. The sulfur compound is suitably a thiol, for example an alkylthiol having 1-12 carbon atoms, or an arylthiol such as a thiophenol. The sulfur compound may be a thioamide, for example thiourea or thioacetamide, especially if capable of forming a thiol-imide structure. Polythiols may be used.

The metal-containing sorbent may include a support similar to that of the sulfur compound. Metal may be applied to the support by for example vapour-phase deposition, impregnation with pre-formed colloidal metal or impregnation with a solution or suspension of a compound, followed by metal-formation by heating or chemical reduction. Gold appears to be very effective as the metal; it may be impregnated in plating conditions. Typically the content of gold is in the lower part of the range specified below.

The sorbent may be present in a fixed random or monolithic bed or a movable, e.g. fluidised bed.

In addition to the above treatment, the feedstock may be contacted with sulfur in an active state as metal polysulfide and/or sulfide of metal in one or more of its higher valency states. It may comprise elemental sulfur. The active material of the sorbent is preferably based on at least one transition metal from groups IB, IIIA to VIIA and VIII of the Periodic Table shown in Pure and Applied Chemistry (1971) vol 28, page 11 quoted in the European Patents Handbook Part I Chapter 6.16.4 (1983).

Two classes of sorbent appear to be relevant to the process. The sorbent characterising the invention is a 'supported sorbent' which typically contain 0.1-40, for example 5-40, % of active materials, balance support material. The above metal(poly) sulfide sorbent is a 'rich' sorbent, typically containing 40-95, for example 40-70, % of active material, balance support material. The active material of rich sorbent may comprise other sulfides and/or sulfidable oxides such as zinc oxide. The support material may comprise one or more oxides usable as catalyst supports, for example alumina, silica, titania, zirconia and chromia, free or in combinations such as aluminosilicates (e.g. clays or zeolites) and hydraulic cement. The active material of such optional supported sorbent may be for example the sulfided oxide of nickel and/or cobalt (2-10%), or molybdenum (5-20%), or a mixture of these; the support oxide is

suitably alumina. The active material (calculated as oxides) of rich sorbents is exemplified by 55-65% of copper oxide CuO with 20-30% of zinc oxide, with up to 20%, on the copper oxide and zinc oxide, of alumina as support oxide. The surface area of rich sorbents is typically in the range 20-250m²/g.

The conditions of operation of the process are typically:

pressure 1-120 bar abs;

residence time 2-20 sec for gas or 2-20 min for liquid.

temperature 0-300C, especially 10-200C.

The purification is preferably operated in two or more stages differing in temperature within those ranges, typically 0-50C for the low-temperature (LT) stage and 80-200C for the high temperature (HT) stage. Preferably the HT stage precedes the LT stage, to effect decomposition of any organo-mercury compounds ahead of final sorption of mercury.

A combination in which a stage using 'rich' sorbent precedes or follows a stage according to the invention is preferred.

A plurality of reactors may be disposed in parallel with switching valves to permit purification to continue in one reactor while another is being discharged and recharged. Each reactor may be subdivided or duplicated with piping connections for operation on a lead/lag basis, that is, may comprise two series-connected interchangeable independently rechargeable parts, with by-passes and switching valves to permit mercury-rich fresh hydrocarbon to be fed to partly-spent sorbent before contacting fresh sorbent.

The process or combination may be operated in combination with one or more other purification steps. These may include gross-impurity removal, for example fractionation, drying and hydrogenative purifications such as desulfurisation. More particularly the other steps may comprise arsenic removal, for example by contacting with lead oxide, for example 20-30% (as PbO) on alumina. In another example the process according to the invention is operated in combination with purification at a similar or different temperature by contact with a similar or different mercury sorbent, preferably copper oxide/zinc oxide as mentioned above or possibly the known sorbent active carbon, any of which may contain sulfur to promote sorption of mercury.

The feedstock in contact with the sorbent can be gaseous or liquid, for example vaporised or vaporisable liquid or vapour/liquid mixture, depending on pressure and temperature of operation. Raw or partly purified natural gas feed to liquefaction is an important example,

owing to the effect of mercury on the aluminium heat exchangers of the liquefaction plant. Another important feedstock is ethylene cracker raw material such as ethane, NGL, LPG or naphtha, since separation of the cracked product is cryogenic. Such processes in combination with feed pretreatment according to the invention constitute further aspects of the invention.

Higher hydrocarbons are normally present in natural gas obtained from gas wells. These higher hydrocarbons in the gas have to be removed prior to liquefaction of the gas or feeding to long gas pipeline. The separated liquid higher hydrocarbons, known as 'condensate' or 'natural gas liquids' (NGL) are stabilised and sold for further treatment. They are similar to light crude oil and are distilled in a series of columns to produce various fractions, in particular LPG, light naphtha, heavy naphtha, kerosene, gas oil and fuel oil. The process of the invention can be integrated as described below into the condensate treatment process to remove mercury, if present regularly or occasionally.

In a particular process according to the invention the mercury removal is operated in combination with the stages of pre-cut, debutanisation and condensate splitting, to produce at least one of the fractions LPG, light naphtha, heavy naphtha, kerosene and fuel oil, each substantially free of mercury. Further, the invention provides a process of producing ethylene by thermal cracking of hydrocarbon feedstock and cryogenic separation of the product, characterised by subjecting the feedstock to mercury removal as herein described.

The feedstock may contain enough sulfur compound to load and maintain the solid sorbent from an initial state. If desired, the sorbent may be pre-loaded, for example by contacting with sulfur compound. If the feedstock has previously been strongly desulfurised, a feed of sulfur compound may be made continuously or intermittently to maintain the sorbent.

The feedstock in contact with the sorbent is preferably substantially water-free, typically having a water dew-point under 4°C. it is also preferably substantially free of hydrogen.

The capacity for mercury of the sorbent per unit volume can be greater than that of the activated carbon. In addition, the volume of sorbent exposed to the feedstock is preferably greater, e.g. by a factor of 2 to 4, than that of the carbon. Consequently, at a convenient reactor volume, the sorbent need be changed less often than when using carbon alone.

Referring to figure 1 of the drawings, a preferred plant for carrying out the process comprises high temperature (HT) reactor 10 typically in the range 80-200°C and low temperature (LT) reactor 20 typically in the range 15-50°C. Each reactor includes (not shown) a sorbent charging port and discharge port; and each may be connected for lead/lag operation as described

above. Each reactor has respectively feedstock inlet 12, 22 and product outlet 14, 24. For reactor 10 inlet 12 is fed with fluid that has entered at 28, has been warmed in feed/effluent heat exchanger 16 and has been brought to reaction temperature in heater 18 heated by steam or combustion gases. Reactor 10 contains a bed of sorbent to be described. For reactor 20 inlet 22 is fed with fluid that has been brought to reaction temperature in water-cooled heat exchanger 26. Reactor 20 contains upper and lower sorbent beds to be described.

In HT reactor 10 the sorbent (30) is for example copper oxide-zinc oxide-alumina, pre-sulfided. In LT reactor 20 the upper bed (32) contains silica-supported thiophenol or gold and the lower bed 34 is charged with alumina-supported lead oxide.

The plant functions as follows. Feedstock, typically from gross purification or from activated carbon treatment, entering at 28 is warmed in feed/effluent heat exchanger 16, heated further heated at 18 and fed into HT reactor 10 at 12. In bed 30 mercury and volatile compounds thereof are immobilised, apparently by conversion to mercuric sulfide under the catalytic effect of the sulfided sorbent. The product of HT reactor 10 passes through the hot side of heat exchanger 16 and is cooled at 26 to the inlet temperature of LT reactor 20, which it enters at 22. In bed 32 further traces, if any, of mercury are removed. In bed 34 any traces of arsenic are removed. The product of LT reactor 20 passes out at 24 to a user. Figure 3 shows the process of fig.1 as applied to condensate treatment with appropriate minor modifications.

Referring to figure 2 of the drawings, a preferred plant for carrying out the process comprises LT reactor 110 and HT reactor 120. Each reactor includes (not shown) a sorbent charging port and discharge port; and each may be subdivided and connected for lead/lag operation as described above. Each reactor has respectively feedstock inlet 112, 122 and product outlet 114, 124. For LT reactor 110 inlet 112 is fed with fluid that has entered at 128 at ambient temperature. LT reactor 110 contains an upper and a lower bed of sorbent to be described. For HT reactor 120 inlet 122 is fed with fluid from 114 that has been warmed in feed/effluent heat exchanger 116 and brought to reaction temperature in exchanger 126 heated by steam or combustion gases. HT reactor 120 contains a sorbent bed to be described.

In LT reactor 110 the upper bed (132) contains pre-sulfided copper oxide/zinc oxide/alumina and the lower bed 134 is charged with alumina-supported lead oxide. In HT reactor 120 the sorbent (130) is for example silica-supported thiophenol or gold.

The plant functions as follows. Feedstock, typically from gross sulfur removal or activated carbon treatment, entering at 128 passes into LT reactor 110 at 112 and is freed of low-

temperature-active mercury in bed 132, and of arsenic compounds in bed 134. The product, containing any residual mercury compounds, is warmed by passing through the cold side of feed/effluent heat exchanger 116, then heated at 126 to the inlet temperature of HT reactor 120, which it enters at 122. In bed 130 the mercury and volatile compounds thereof remaining after bed 120 are immobilised, apparently by conversion to mercuric sulfide or amalgam. The product of HT reactor 120 passes out at 124 to a user.

Referring to fig.3 showing the process of fig.1 as applied to condensate treatment, HT reactor 10 feeds direct to the first condensate distillation column 340 ('precut column') without heat exchanger 16.. The overhead of column 340 is fed to debutaniser column 342, in which it is resolved into overhead LPG 344 and bottoms 346. LPG 344 is passed out to a user accepting single-stage mercury removal. Bottoms 346 is cool and is fed to (first) LT reactor 20 without heat exchanger 26. The product of (first) LT reactor 20 is a light naphtha substantially free of mercury. The bottoms of column 340 is fed to condensate splitter column 350, in which it is resolved into overhead 352 and bottoms 358. Overhead 352 is cooled in heat exchanger 26 and fed to (second) LT reactor 20, to give a heavy naphtha substantially free of mercury. Bottoms 358 is a fuel oil passed out to a user accepting single-stage mercury removal. Both LPG 344 and fuel oil 358 are products of HT mercury removal by the process of the invention.

The process of fig 2 can be integrated analogously into a process scheme.

CLAIMS

1. A process for purification of hydrocarbons characterised by removing mercury by contact with a solid sorbent comprising an organic sulfur compound and/or a metal capable of amalgamation with mercury.
2. A process according to claim 1 in which the sulfur compound-containing sorbent is characterised by:
 - (i) support of surface area in the range $50-500 \text{ m}^2 \text{ g}^{-1}$; and
 - (ii) sulfur compound exerting low vapour pressure at the temperature at which the process is to be operated by virtue of high boiling point or strong physical or chemical sorption.
3. A process according to claim 2 in which the support is silica.
4. A process according to any one of the preceding claims in which the sulfur compound is: an alkylthiol having 1-12 carbon atoms, or an arylthiol or a polythiol; or a thioamide capable of forming a thiol-imide structure.
5. A process according to any one of the preceding claims in which the metal-containing sorbent includes a support similar to that of the sulfur compound.
6. A process according to any one of the preceding claims in which metal is applied to the support by for vapour-phase deposition, impregnation with pre-formed colloidal metal or impregnation with a solution or suspension of a compound, followed by metal-formation by heating or chemical reduction.
7. A process according to any one of the preceding claims in which the metal is gold.
8. A process according to any one of the preceding claims including also contacting the feedstock with sulfur in an active state as metal polysulfide and/or sulfide of metal in one or more of its higher valency states or as elemental sulfur.
9. A process according to claim 8 in which the active material of the sorbent is based on at least one transition metal from groups IB, IIIA to VIIA and VIII of the Periodic Table shown in Pure and Applied Chemistry (1971) vol 28, page 11 quoted in the European Patents Handbook Part I Chapter 6.16.4 (1983).
10. A process according to claims 1 to 7 in which the sorbent is a supported sorbent containing 0.1-40% of active materials, balance support material.
11. A process according to claim 8 or claim 9 in which the sorbent is a rich sorbent containing 40-95% of active material, balance support material.

12. A process according to claim 9 or claim 11 in which the active material of such supported sorbent is the sulfided oxide of nickel and/or cobalt (2-10%), or molybdenum (5-20%), or a mixture of these; the support oxide is suitably alumina.
13. A process according to claim 11 in which (calculated as oxides) the rich sorbent comprises 55-65% of copper oxide CuO with 20-30% of zinc oxide, with up to 20%, on the copper oxide and zinc oxide, of alumina as support oxide.
14. A process according to claim 11 or claim 13 in which the surface area of the rich sorbent is in the range 20-250 m²g⁻¹.
15. A process according to any one of the preceding claims in which the feedstock in contact with the sorbent is:
 - vaporised or vaporisable liquid or vapour/liquid mixture raw or partly purified natural gas feed to liquefaction; or
 - ethylene cracker raw material ethane, NGL, LPG or naphtha.
16. A process according to any one of the preceding claims operated in combination with the stages of pre-cut, debutanisation and condensate splitting, to produce at least one of the fractions LPG, light naphtha, heavy naphtha, kerosene and fuel oil, each substantially free of mercury.
17. A process according to any one of the preceding claims in which the feedstock in contact with the sorbent has a water dew-point under 4C.
18. A process according to any one of the preceding claims in which the feedstock in contact with the sorbent is also substantially free of hydrogen.
19. A process according to any one of the preceding claims in which purification is effected in two or more stages differing in temperature, in the range 0-50C for the low-temperature (LT) stage and in the range 80-200C for the high temperature (HT) stage.
20. A process according to claim 19 in which the HT stage precedes the LT stage.
21. A process according to claim 20 in which the HT stage uses a rich sorbent and the LT stage is as claimed in any one of claims 1 to 7 and 10.
22. A process according to claim 20 in which:
 - an HT reactor contains pre-sulfided copper oxide/zinc oxide/alumina; and
 - an LT reactor comprises an upstream bed containing silica-supported thiophenol or gold and a downstream lower bed containing alumina-supported lead oxide.
23. A process for purification of hydrocarbons, substantially as herein described with reference to the foregoing drawings and specific description.



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Application No: GB 0304062.3
Claims searched: 1-23

Examiner: Fiona Warner
Date of search: 6 August 2003

Patents Act 1977 : Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance	
X	X=1,5 & 7 at least	US 5141724 A	(MOBIL) see in particular column 2, lines 26-33; column 3, lines 42-52; column 4, lines 23-28; column 5, lines 20-24
X	1,5 & 6 at least.	US 5053209 A	(MOBIL) see in particular "Summary of Invention"
X	1,5,7 & 9 at least	EP 0381453 A	(MOBIL) see in particular page 1, lines 1-2; lines 25-32 and page 3, lines 14-16
X	1,4 at least	WO 01/62870 A1	(UNION OIL) see in particular "Summary of Invention"; page 7, lines 10-17
A,P		GB 2365874 A	(WCP)
A		EP 0357873 A1	(JGC)
A		US 4094777 A	(INSTITUT FRANCAIS DU PETROLE)
A		US 4474896 A	(UNION CARBIDE)

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X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^v:

C5E

Worldwide search of patent documents classified in the following areas of the IPC[?]:

C10G; B01D; B01J

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INVESTOR IN PEOPLE

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The following online and other databases have been used in the preparation of this search report:

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